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Regenerated Lignocellulose Fibers Spun from Willow Lignin and Cellulose blends using Ionic Liquid Solvents.

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ABSTRACT: We report a method to extract lignin from willow, using triethyl ammonium hydrogen sulphate [Et3NH][HSO4. This method is used to manufacture fibers with a range of compositions.. This extraction achieved an 18% yield of lignin as characterized by ATR-IR and elemental analysis indicated a high carbon yield. 1-Ethyl-3-methylimidazolium acetate [C2C1im][OAc] was then used as a solvent to manufacture lignin-cellulose fiber blends. The Young's modulus of a 75:25 lignin:cellulose fiber was found to be 3.0 ±0.5 GPa which increased to 5.9 ±0.6 GPa for a 25:75 lignin:cellulose blend. From a characterization of the surface morphology using Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) it was observed that a rich lignin content in the fiber blend increased the surface roughness. FT-IR analysis confirmed the presence of aromatic groups of lignin from the presence of peaks located at ~1505 cm^{-1} and ~1607 cm^{-1}. The presence of lignin improves the thermal stability of the fiber blends by allowing them degrade over a wider temperature range. This is potentially useful for the utilisation of renewable lignocellulosic biomass derived fibers as carbon fiber precursors. Although the mechanical properties of the regenerated fibers were diminished by the addition of lignin, the blends prepared produced a solution suitablefor a stable fiber spinning process.

INTRODUCTION

Given concerns over our dependence on petroleum to derive polymeric materials, in the form of fibers and resins, there is a need to develop more sustainable manufacturing routes[1]. Glass fibre processing requires high temperatures in the production process. High performance carbon fibers are predominantly manufactured using non-renewable polyacrylonitrile (PAN) precursors. Lignocellulose biomass-derived regenerated fibers are a promising alternative to replace glass fibers, due to their lower density, and non-renewable PAN based precursors for the production of carbon fibers. Willow is a well-established, historically cultivated crop that shows promise as a source of lignocellulose (lignin, cellulose and hemicellulose) biomass that can be effectively utilised as a renewable resource for making fibers or resins for renewable polymer composite applications.

Due to its high carbon content, lignin has been explored as a precursor for making carbon fibers [2-4], However the processing of lignin to manufacture carbon fibers is difficult, often requiring chemical modification [2]. To facilitate the spinning of lignin based fibers, researchers have blended the material with synthetic non-renewable polymers such as polypropylene (PP), poly (ethylene oxide) (PEO) and poly(ethylene terephthalate) (PET) [5]. These synthetic polymers are reported to improve the spinnability of lignin by increasing its viscoelastic properties [5].

Cellulose is a potentially sustainable and renewable replacement for synthetic polymers [6-7]. Cellulose is however known to have a low carbon yield when graphitized. Therefore, there is a potential to blend lignin with cellulose to

improve this carbon yield. Blending lignin with cellulose is possible as polar functional groups such as hydroxyl and carbonyl groups allow interaction between the two materials [7-8].

Ionic liquids (ILs) are solvents purely composed of ions [9-10]. The ability of ILs to dissolve cellulose efficiently relies on the fact that the anion has a high hydrogen bond acceptability [11-12]. ILs are also known to dissolve other biopolymers, particularly lignin itself, as well as lignocellulose biomass [11, 13-14]. These developments have opened up opportunities to use ILs as solvents for blending cellulose and lignin to prepare completely sustainable/renewable fibers and as potential precursors for carbon filaments. In this work, fibers with different ratios of lignin (derived from willow) to cellulose were developed using ILs. Lignin-cellulose solutions in ILs are spun into regenerated fibers using a dry-jet wet fiber spinning method. The manufacturing method developed in this study for regenerated-lignin cellulose fibers offers an attractive approach to utilise the willow lignin as a renewable feedstock for composite materials.

EXPERIMENTAL METHODS

Materials

1-Ethyl-3-methylimidazolium acetate [C_2C_1im][OAc] was purchased from Sigma-Aldrich (Dorset, UK). Cellulose pulp sheets were supplied by Rayonier Inc, (Fernandina Beach, USA) with a degree of polymerization of 890. These cellulose pulps were first cut into small pieces and ground before they were used in the dissolution process. Triethylammonium hydrogen sulphate [Et_3NH][HSO_4] was synthesized by a drop-wise addition of 5 M H_2SO_4 to Et_3N using an acid: base ratio of 1:1. An ice bath was used to maintain the temperature. The mixture was stirred for 24 h and dried under vacuum. The H_2SO_4 was titrated prior to use in order to determine its concentration as the acid-base ratio has a large impact upon pre-treatment [15].

Pre-treatment

Willow lignin, water and [Et_3NH][HSO_4] were homogeneously mixed in a 1:2:8 mass ratio. The mixtures were subjected to a temperature of 120 °C for 22 h. The resulting solution (black liquor) was filtered using Whatman 542 filter paper and washed with 3 volumes of ethanol. The ethanol of the black liquor was evaporated under vacuum at 55 °C. The residual lignin was precipitated through the addition of 2 volumes of distilled water and then centrifuged at 4000 rpm for 15 min. The residual lignin was washed with distilled water and dried at 70 °C overnight.

Preparation of Lignin Biomass-Cellulose Solution

Lignin and cellulose were mixed in different ratios as described in Table 1. Lignin powder was kept in a vacuum oven at 80 °C beforehand to eliminate any moisture before its dissolution. The dissolution of lignin and cellulose in [C_2C_1im][OAc] solution was carried out on a magnetic stirrer hotplate in a fume hood. A total of 8wt% of raw materials were submerged in 40 g of [C_2C_1im][OAc] solution that was suspended in an oil bath. Lignin was dissolved first at a temperature of 110 °C for 48h, after which cellulose was added and the temperature was reduced to 90 °C. This solution was then placed in a vacuum oven for 24 h for degassing.

Fiber Spinning

The lignin-cellulose solutions were placed in the fiber spinning equipment (Rondol, UK) for manufacturing regenerated lignin-cellulose filaments as shown in Figure 1. The solution was extruded into a water bath with a 1 cm air gap between the nozzle and the surface of the water. The solidified fibers were then wound up using a rolling winder. The fibers were then immersed in water for 2 days to wash out any remaining ionic liquid and then dried for 2 days at room temperature.

Fluorescence microscopy

Images of lignin-cellulose fibers were obtained using a Leica DMI 3000B fluorescence microscope (Leica Microsystems CMS GmbH, Wetzlar, Germany). The fiber diameters were measured using ImageJ software.

Fourier transform infrared (FT-IR)

FT-IR spectra of lignin-cellulose fibers were obtained using a Spectrum 100 FT-IR Spectrometer (Perkin-Elmer, USA) within a wavenumber range of 650-4000 cm^{-1} in transmittance mode and at resolution of $4cm^{-1}$. All samples were scanned repeatedly at three different locations for each specimen.

Field-Emission Scanning Electron Microscopy (FE-SEM)

The morphologies and cross-sections of the fibers were observed using a JEOL IT300 (Boston, USA) field emission gun scanning electron microscope. A 1 cm length of fibers was cut from each sample and mounted on a sample holder. The samples were sputter coated with a 15 nm thick silver coating.

Mechanical Properties

Mechanical testing of the fibers was carried out using a Dia-stron LEX820 single fiber tester (Hampshire, UK) coupled to a 20 N load cell, with a strain rate of 2 mm per min^{-1}. The fibers were cut and mounted on a 2 cm gauge length sample holder and the tensile testing was carried out at room temperature. A total of 5 samples were tested for each specimen.

Lignin content characterization

The purity of lignin samples was determined based on modified TAPPI standards (T222 om-83 and T249 cm-85). Each dry fibre sample was pre-hydrolysed for 1 hour with 72% v/v sulphuric acid in a thermostatic bath at 30 ºC. Then deionised water was added in order to dilute samples up to 4% sulphuric acid. Samples were then hydrolysed for 3 hours at 100 ºC, and afterwards ice cooled. The acid insoluble fraction of lignin (IL) samples (Klason lignin) was separated by filtration (glass microfiber filters 245 Whatman), washed with deionised water until neutral pH was achieved and oven-dried at 105 ± 3 ºC. The Klason lignin content of each sample corresponded to the acid insoluble fraction gravimetrically determined. From each experiment, the resulting hydrolyses were reserved for the subsequent acid soluble lignin (ASL) determination by UV-vis spectrometry.

Stabilization and Carbonisation

Stabilization of the precursor involves decomposition and rearrangement of the polymer in an oxidative atmosphere. Thermogravimetric analysis (TGA) of cellulose fibers performed in air by Tang and Bacon [16] has shown that significant pyrolytic degradation begins at 240 °C, and therefore, stabilization of lignocellulose fibers were carried out at this temperature. Lignocellulose fibers were initially stabilized by heating to 240 °C in air at a rate of 5 °C min^{-1}, followed by a 30-min isotherm at the final maximum temperature. These stabilized fibers were then carbonized by heating to 1000 °C in an Argon atmosphere at a rate of 10 °C min^{-1}, followed by a 60-min isotherm at the final maximum temperature.

Raman Characterization of Fibers

Raman spectra of carbonised fibers were obtained using a Renishaw 1000 Raman imaging microscope equipped with a thermoelectrically cooled CCD detector. A laser with a wavelength of 532 nm was used to record spectra from fibers using an exposure time of 10s and five accumulations. The laser intensity was reduced to 10% and the beam was focused using a ×50 objective lens onto a few carbon fibers.

Atomic Force Microscopy (AFM) Characterization

Fibers were embedded in a resin, then cut and polished to provide a clean cross-section for characterization using AFM. Measurements were conducted using a Multi-mode VIII microscope with Nanoscope V controller and PeakForce feedback control (Bruker, Santa Barbara, CA, USA). SCANASYST-HR cantilevers, of nominal tip radius 2 nm, were utilised in combination with a fast scan head unit to resolve the morphology of the fiber over 1×1 µm and 10×10 µm regions. The RMS roughness of each fiber cross-section then provided a means to compare the degree of phase separation in each blend [8].

RESULTS

Surface morphology of cellulose and lignin cellulose blends

Figure 2 shows images of the regenerated fibers spun from neat cellulose and lignin-cellulose blends. Lignin changed the colour of the fibres to black, but there was no significant difference in the colour shades with every incremental increase in content. Figures 3(a-d) show images of the surface morphology of pure cellulose, Li:Cell 25:75, Li:Cell 50:50 and Li:Cell 75:25 fibres respectively at ×100 and ×2000 magnifications. Pure cellulose gave a smooth textured fiber (Figure 3a). Figures 3(b-d) indicate that the surface roughness of the fibers increased with an increasing lignin content. This increase in roughness might be due to an increase in defects which possibly leads to a decrease in mechanical properties; fibers are found to transition from a ductile to brittle behaviour.

FT-IR of lignin-cellulose blends

Through ATR-IR characterization, the chemical structures of pure cellulose, pure lignin and lignin-cellulose blends were analysed as shown in Figures 4a and 4b. The spectra for pure cellulose and lignin were compared. The main bands of cellulose and lignin were assigned to functional groups which are shown in Tables 2 and 3 respectively. The main characteristic bands for lignin are located at ~1607 and ~1514 cm^{-1}, which are assigned to aromatic skeletal vibrations [17]. Those bands are present in all the lignin-cellulose blends; the intensity of this band was higher for Li:Cell 50:50 and Li:Cell 75:25 than for Li:Cell 25:75 due to a lower lignin concentration in the latter. One of the distinctive bands observed for lignin is located at ~1694 cm^{-1} assigned to CO in unconjugated ketones, carbonyl and ester groups that are not present for pure cellulose. This band was not observed in the spectrum for the lignin-cellulose fibers due to the formation of hydrogen bonding between lignin and cellulose [18-19]. There is a very intense band located at ~1030 cm^{-1} assigned to C-O stretching whichwas observed for all the fibers. However, this band is modified by the presence of lignin, shifting to a lower wavenumber position [20].

Mechanical properties

Figure 5 presents the stress-strain curves of fibers of pure cellulose and lignin-cellulose blends. The tensile strength, strain at break and Young's modulus of these fibers are summarized in Table 4.From the curves, it is observed that pure cellulose demonstrated ductile behaviour, as indicated by a high strain at break of ~13%. Fibers however became more brittle upon the addition of lignin; strain at break decreased progressively from ~10%, to ~2% for an increase in lignin content from 25% to 75%. This decrease in ductility may be due to an increase in the occurrence of defects in the fibers on the addition of lignin.

The tensile strengths of the fibers also reduce with an increasing lignin content: pure cellulose fiber, ~152 MPa;

Li25% Cell 75%, ~127 MPa; ~84 MPa and Li:Cell 75:25, ~30 MPa (Figure 6a). These fiber strengths are much higher than reported values for pure lignin of ~19 MPa (Alcell lignin) and ~23 MPa (hardwood Kraft lignin) [21]. A decrease in Young's modulus is observed with an increasing lignin content in the fiber blends. The highest content of lignin in the fiber blends yields a Young's modulus of only ~3 GPa. This value increasesaccordingly to ~5 GPa and ~6 GPa with every 25 wt% of lignin reduction (Figure 6b). This increase suggests that cellulose provides stiffness and strength into the fiber blends while lignin provides carbon content. As a carbon fiber precursor, the material ought to have both properties; high mechanical properties and high carbon content. The main objectives of the present study are to produce lignin-cellulose fiber blends with optimal properties as an alternative material for both pure lignin and pure cellulose carbon fiber precursors. Using this blending method we are able to effectively control lignin content, for a continuous filament, which has advantages over using typical plant fibers with limited and fixed lignin contents and lengths. In this study the average diameter of the fibers (Table 4) were found to be similar. It may be possible to produce finer diameter fibers, thus further improving strength if a sufficiently high dope viscosity can be obtained.

Elemental Analysis

One of the main aims of the addition of lignin to cellulose fibers is to increase the carbon content for potential use as a precursor for carbon fibers, as lignin has higher carbon content than cellulose. Elemental analysis was carried out to determine the carbon content and the results are shown in Table 5. From the analysis, it was observed that the presence of lignin increased the carbon content from 42 to 50.

Lignin content

The fibers were subjected to a lignin purity test in order to establish its concentration. The results of this analysis are presented in Table 6. It was observed that the fibers were indeed composed of both lignin and cellulose. The effectiveness of the incorporation of lignin into the fibre was reduced when the content of lignin in the fibers increased; this can be observed for a Li:Cell 50:50 fiber that has a lignin content at ~43% and Li:Cell 75:25 at ~60%.

AFM Characterization

The surface roughness of cross-sections of pure cellulose fibers and respective lignin-cellulose blends was investigated using AFM (Figure 7). A pure cellulose fiber has RMS roughness value of ~19nm that indicatesa smoother surface topography dominating the surface morphology as shown in Figure 7a. The addition of lignin results in distinctive changes in the surface roughness indicated by the uneven topography, as the RMS roughness value increased from ~19nm to a value in the range of 24-38 nm as can be observed in Figures 7b-d. This increase in the RMS surface roughness is possibly due to the presence of lignin.

Characterization of Carbonised Fibers

The structure of the carbonised fibers was characterized using Raman spectroscopy. As shown in Figure 8a, two first-order Raman bands were observed in the region between 1000 cm^{-1} and 3000 cm^{-1}. These bands are the D band at ~1340 cm^{-1} and the G band at ~1590 cm^{-1}. The G band is related to an in-plane bond stretching motion of sp^2-hybridized carbon atoms and the D band is thought to arise from the breathing mode of the aromatic ring near the basal edge [22].

The intensity ratio between the D and G bands (I_D/I_G) has been previously utilized to characterize different forms of carbon materials [23]. As shown in Fig 8b, the I_D/I_G ratio as a function of lignin content is lower than the the values observed for other carbon fibers carbonised from regenerated cellulose filaments under the same temperature regimes. Lower I_D/I_G ratios in the present study indicate structural purity and lack of defects in the structure.

The carbon yield of lignocellulose fibers were calculated using the equation,

$$\text{Carbon yield}\,(\%) = \frac{\text{Weight of carbon fibers}}{\text{Initial weight of lignocellu lose fibers}} \times 100 \quad (1)$$

The carbon yield was found to increase with the lignin content of the precursor fibers (Table 7). Carbon yields of 12% and 13% were observed for pure cellulose and Li:Cell 25:75 fibers, respectively. The carbon yield increased to 29% and 35% for Li:Cell 50:50 and Li:Cell 75:25 fibers, respectively. The increased carbon yield of lignocellulose fibers with a higher lignin content can be attributed to an increased amount of carbon present in lignin. This is an improvement when compared to typical carbon yields of other regenerated cellulose fibers (10-30%) [24].

Discussion

Regenerated fibers were obtained by blending cellulose and lignin (derived from willow). Since both components are biodegradable, the composite is also expected to be biodegradable. Lignocellulose-based fibers are widely used as biodegradable fillers. With their environmentally friendly character and some techno-economic advantages, these fibers motivate more and more different industrial sectors to replace traditional fiber types e.g., glass fibers [25]. Ionic liquids have been widely investigated as solvents for biomass processing where good performance on delignification of biomass have been achieved. Initially,

imidazolium ILs were the most used but due to high price, those derived from simple low cost amines [26] have been used with similar yields [27].

In the present work, we used willow lignin and cellulose to produce fibers with a wide range of lignin mixing ratios; namely 75:25, 50:50, and 25:75 lignin:cellulose. These blends were compared to the two pure materials. The blends of these two materials have mechanical properties in the ranges of 3.04 ± 0.48 GPa to 8.31 ± 0.61 GPa for Young's modulus and 29.91 ± 4.48 MPa to 152.45 ± 6.02 MPa for tensile strength, which are improvements in comparison to the brittle nature of lignin alone [28-29]. It has been reported by Mainka *et al.*[18] that the utilization of lignin as a precursor for carbon fibers normally involves at least three steps; washing the lignin powder and drying, followed by pelletizing the lignin powder before it can be used for melt spinning to produce lignin fibers. Others have also reported having to chemically modify lignin powder to improve its functionality [30]. In the present work the procedures can be reduced as we can directly use lignin powder without washing, pelletizing and modifying. Hence, the addition of cellulose to lignin to form fibers improves its processing behaviour and moldability. The development of cellulose fibers is commonly carried out using a wet-spinning process that is known to yield good mechanical properties [31-32]. Hence, the combination of lignin and cellulose can help to develop natural fibers that contain as high lignin contents as possible with moderately good mechanical properties. These mechanical properties can be improved through interfacial bonding between cellulose and lignin. As in the case of plant-based fibres, the wettability of the participant constituents in the fibre composites can affect the flexural strength, toughness and tensile properties. To improve the wettability of fibres, either physical treatment or chemical treatment shall be investigated. The addition of lignin also increases the thermal stability of our fibers. These fibers therefore could be promising candidates for precursors for carbon fibers.

Conclusions

Lignin-cellulose fibers were produced using a wet-spinning technique with different ratios of each material within the blends. The raw lignin and cellulose were prepared into a solution dope and spun into fibers using fixed parameters to allow comparison between the materials. Blends of these two materials produced a spinnable and stable solution. The mechanical properties showed an increase in tensile strength and Young's modulus with an increase in the cellulose weight fraction into the fibers. This performance was expected since cellulose on its own has good mechanical properties. However, the lignin-cellulose fibers produced exhibit better mechanical properties than previously reported pure lignin fibers and those combined with non-renewable synthetic polymers. Our work reports a novel way to utilise lignin from abundantly available biomass sources such as willow to produce fibers with moderately good mechanical properties and good thermal stability which could in principle offer the potential to develop these as renewable precursors for carbon fibers. Our approach contrasts to those that use cellulose alone as a raw material with comparatively lower carbon contents.

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FIGURES

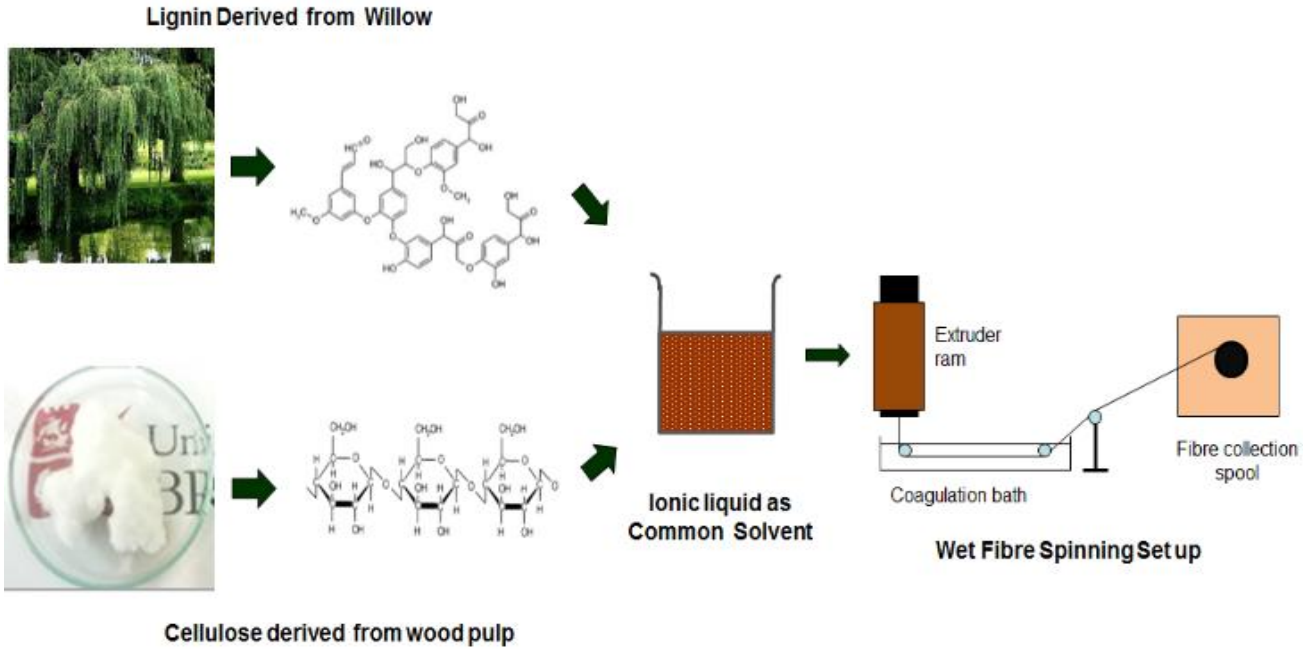


Figure 1. Schematic of the solution preparation and wet spinning process of lignin-cellulose fibers.

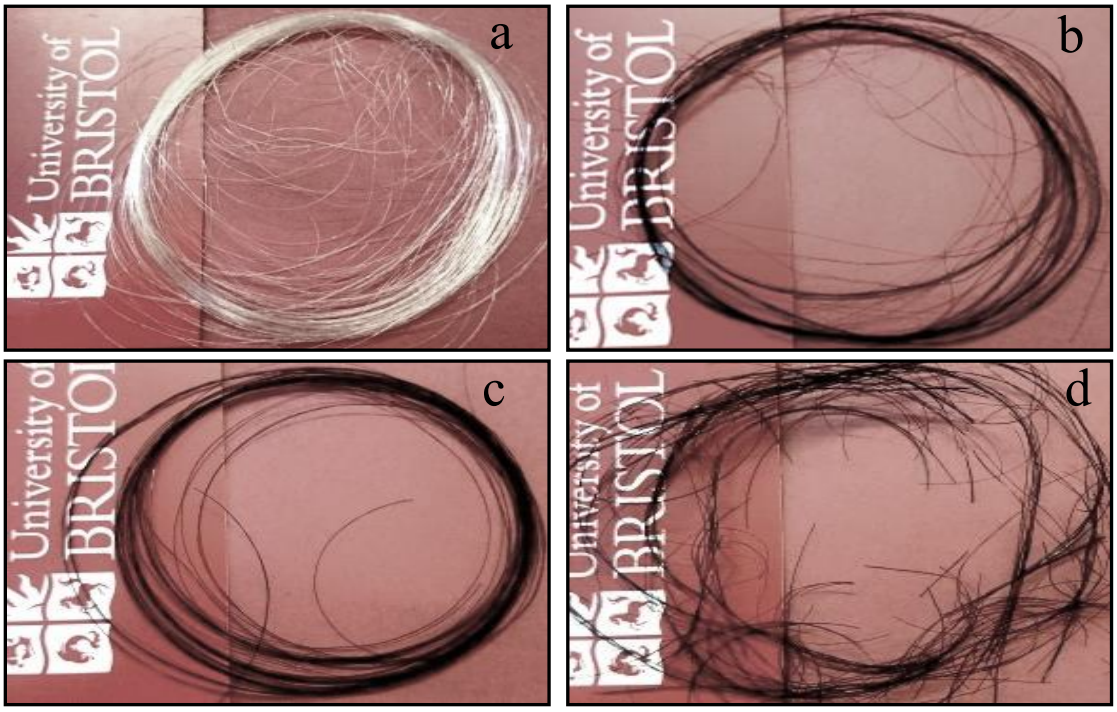
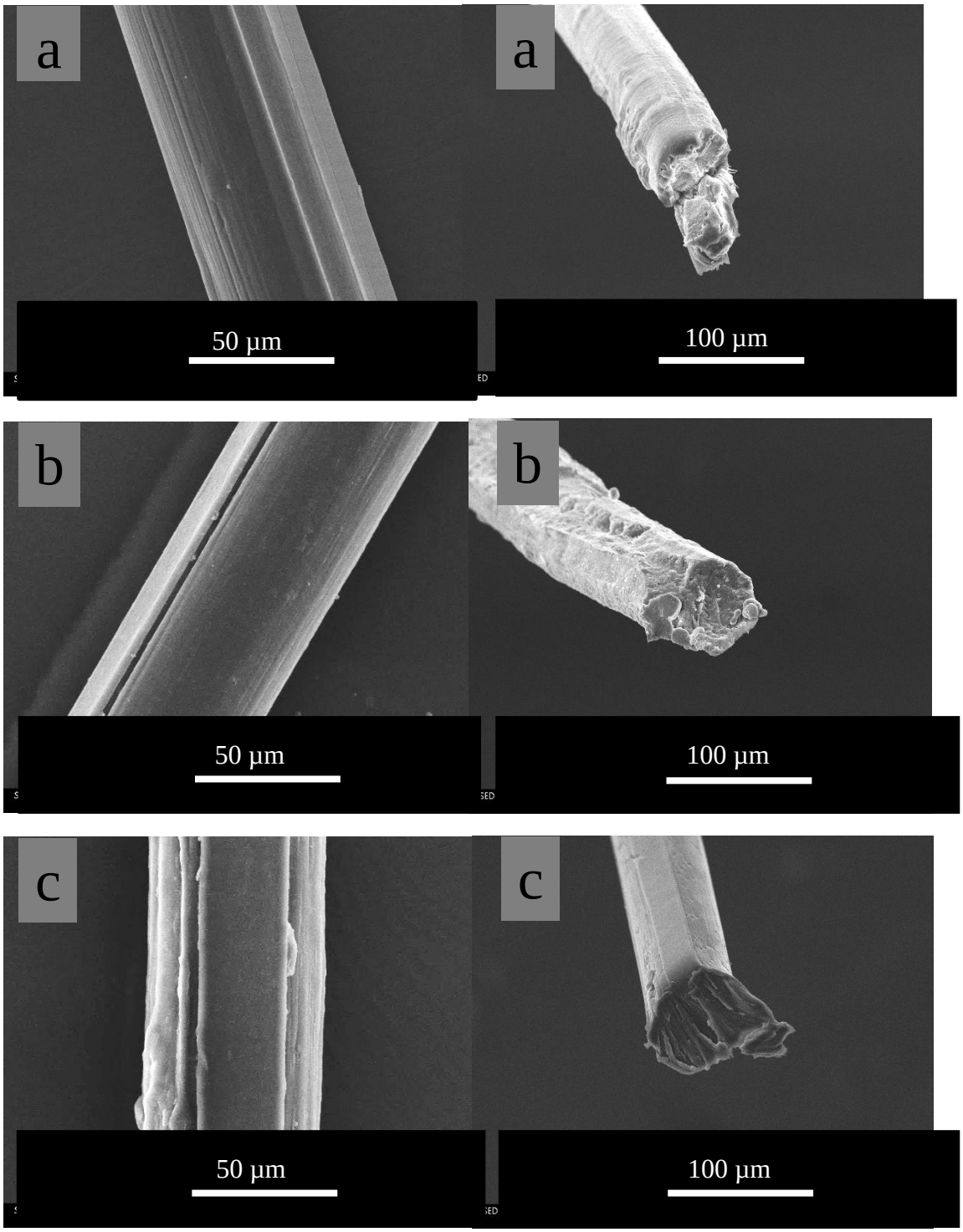


Figure. 2 Typical images of manufactured lignin-cellulose fibers after drying; (a) pure cellulose fiber, (b) Li:Cell 25:75 (c) Li:Cell 50:50 and (d) Li:Cell 75:25, respectively.


a
50 µm
a
100 µm
b
50 µm
b
100 µm
c
50 µm
c
100 µm

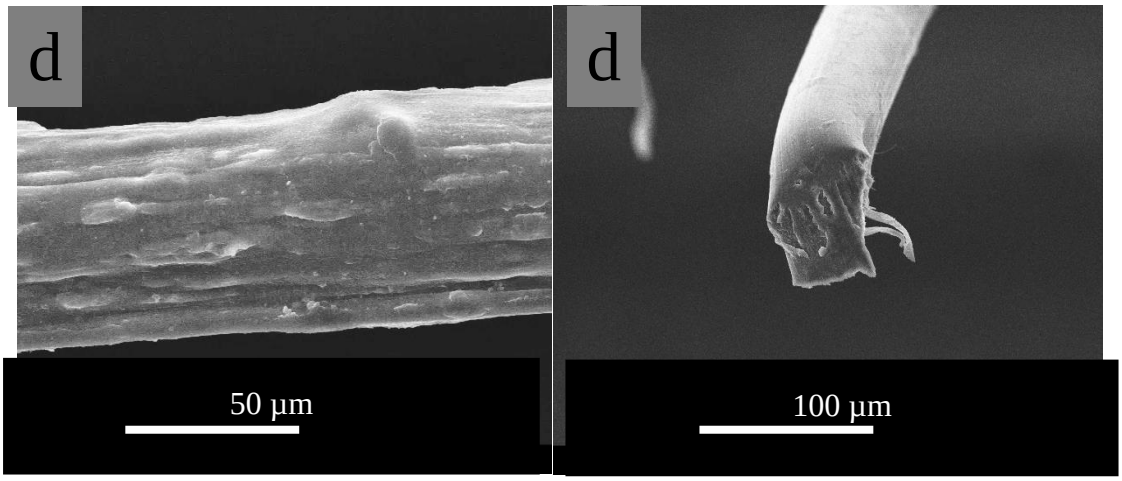


Figure 3. Typical Scanning Electron Microscopy (SEM) images of the surface morphologies (left) and cross-sections (right) of pure cellulose and cellulose-lignin fiber blends at 500× and at 250× magnifications respectively; (a) pure cellulose fiber, (b) Li:Cell 25:75 (c) Li:Cell 50:50 and (d) Li:Cell 75:25, respectively.

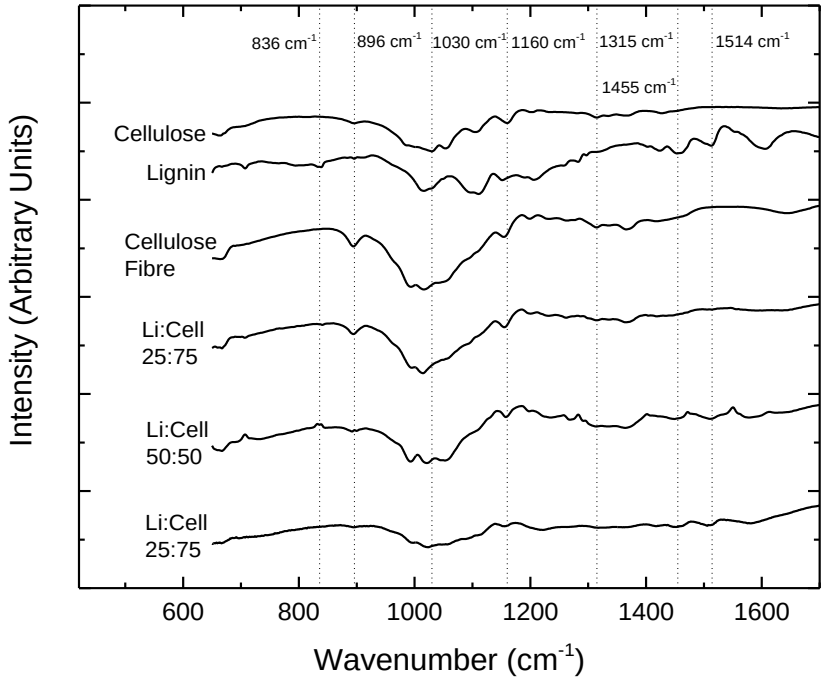


Figure 4a. Typical ATR-IR spectra for a wavenumber range of 2000-600 cm^{-1} for lignin-cellulose blends.

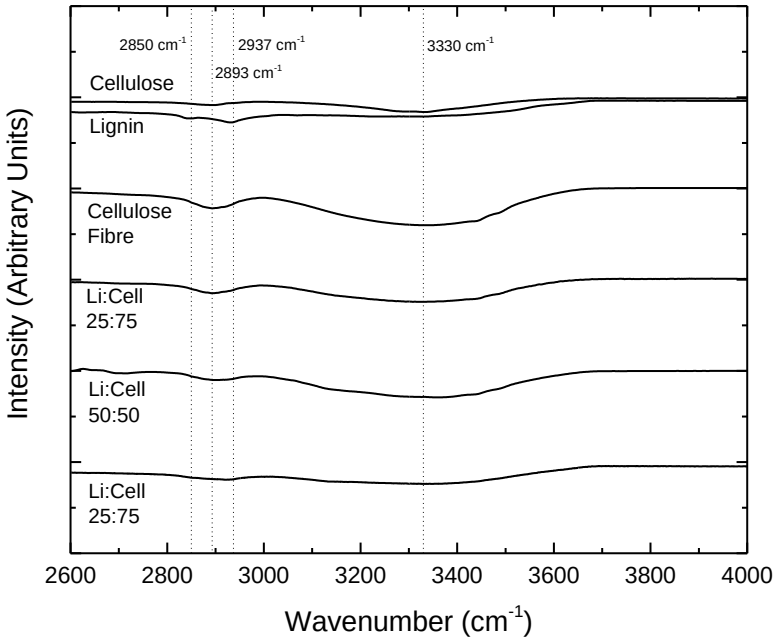


Figure 4b. Typical ATR-IR spectra for a wavenumber range of 4000-2500 cm^{-1} for lignin-cellulose blends.

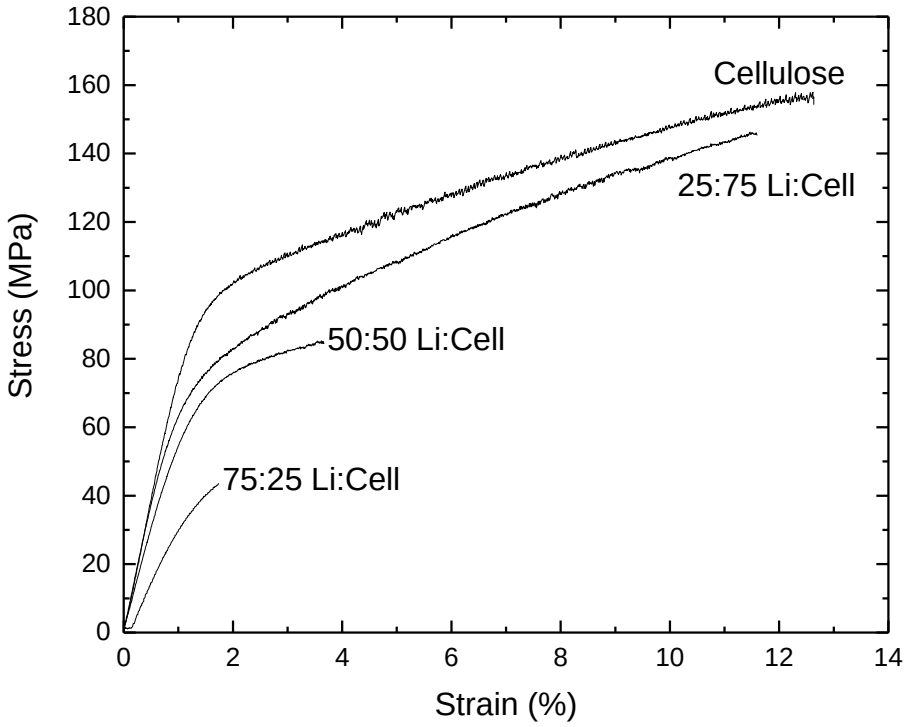


Figure 5. Typical Stress-strain curves for cellulose fibers and their respective lignin-cellulose blends

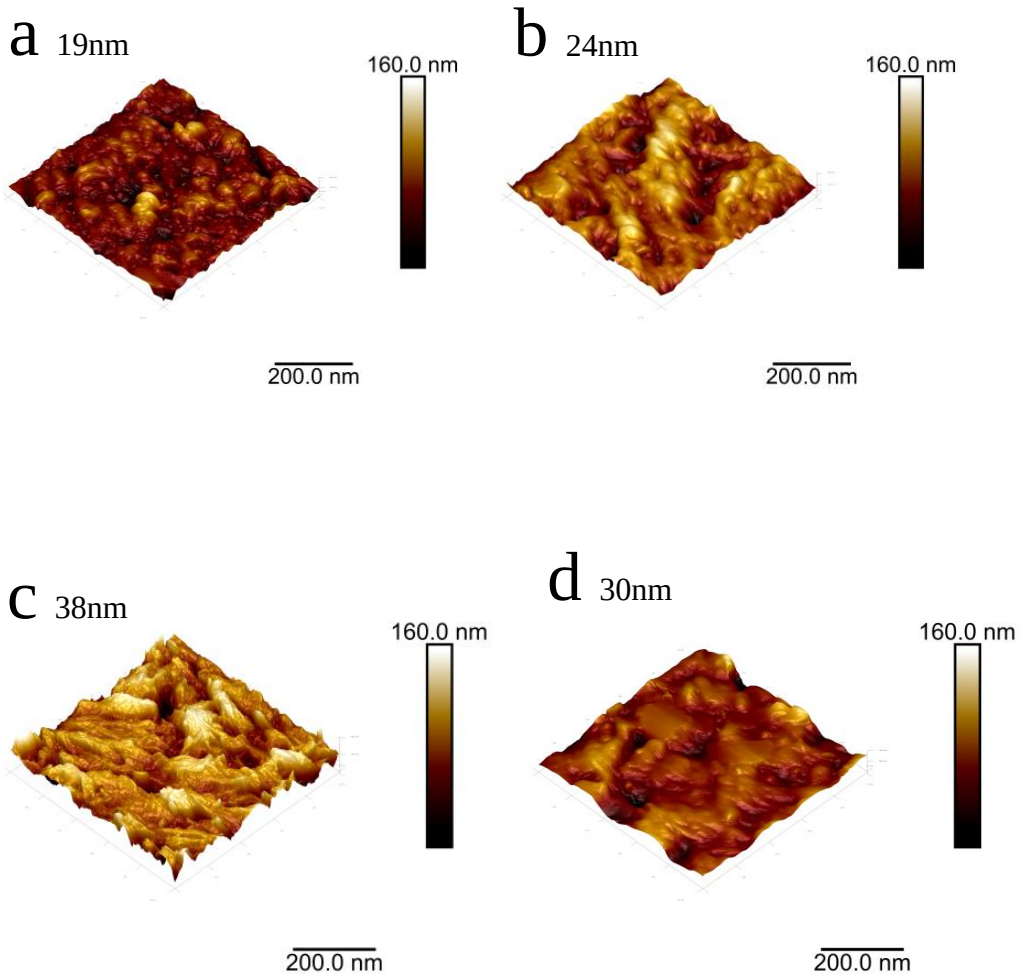


Figure 7. AFM characterization and average surface roughness (nm) for a 1 μm × 1 μm area of (a) a pure cellulose fiber (b) a Li:Cell 25:75 fiber (c) a Li:Cell 50:50 fiber and (d) a Li:Cell 75:25 fiber. Root mean square (RMS) roughness' of the fibers' surfaces are stated in the insets of the images.

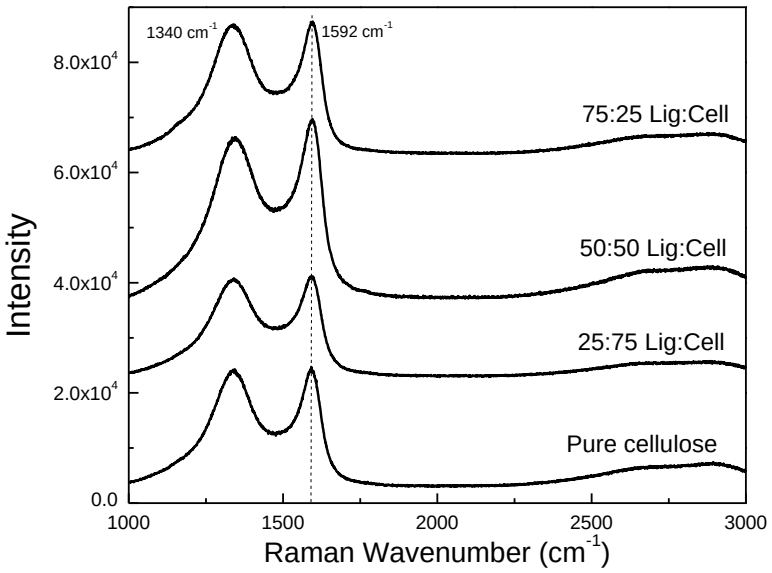


Figure 8a. Typical Raman spectra obtained from lignocellulose fibers with different lignin contents.

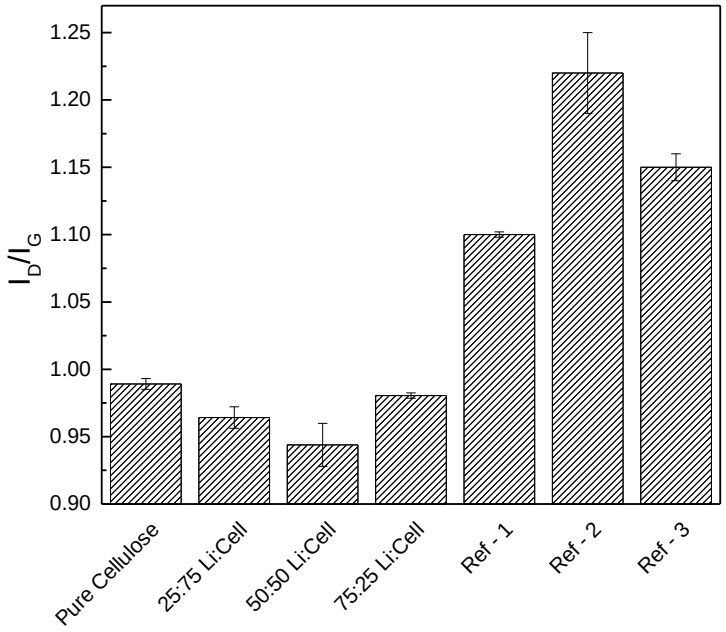


Figure 8b. I_D/I_G ratios of carbonised lignocellulose fibers and other regenerated cellulose fibers obtained from references [33-35].

TABLES

Table 1. Lignin and Cellulose compositions

Sample	Lignin(wt%)	Cellulose (wt%)
Pure cellulose	-	8
Li:Cell 25:75	2	6
Li:Cell 50:50	4	4
Li:Cell 75:25	6	2

Notes: Pure lignin fiber was not prepared as comparison due to the low solution viscosity, and so it was not possible to spin into a fiber.

Table 4.Young's modulus, tensile strength and strain at break of cellulose fibers and their respective cellulose-lignin blends

Samples	Young's modulus (GPa)	Tensile strength (MPa)	Strain at break(%)	Average diameter (μm)
Pure cellulose	8.31 ± 0.61	152.45 ± 6.02	12.89	100.82 ± 2.91
Li:Cell 25:75	5.94 ± 0.63	127.76 ± 9.18	10.02	92.94 ± 2.67
Li:Cell 50:50	5.15 ± 0.40	83.67 ± 4.06	4.32	98.66 ± 4.56
Li:Cell 75:25	3.04 ± 0.48	29.91 ± 4.48	1.55	109.68 ±13.65

Table 5. Elemental analysis

Sample	C	H	N	O	Molecular Formula
Cellulose	42.42 ± 0.07	6.0 ± 0.01	0.1	51.4 ± 0.07	$C_{1.1}H_2O_1N_{0.002}$
Lignin	55.84 ± 0.04	4.80 ± 0.06	1.59 ± 0.02	37.77 ± 0.07	$C_{1.97}H_2O_1N_{0.04}$
Li:Cell 25:75	49.50 ± 0.04	5.32 ± 0.07	2.48 ± 0.09	42.7 ± 0.1	$C_{1.5}H_{1.97}O_1N_{0.06}$
Li:Cell 50:50	49.8 ± 0.05	5.33 ± 0.04	3.31 ± 0.07	41.56 ± 0.09	$C_{1.6}H_{2.03}O_1N_{0.09}$
Li:Cell 75:25	50.65 ± 0.08	5.38 ± 0.05	4.03 ± 0.05	39.9 ± 0.1	$C_{1.69}H_{2.14}O_1N_{0.12}$